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DEVELOPMENT OF A Ge/GaAs HMT TECHNOLOGY BASED ON PLASMA-ENHANCED CHEMICAL VAPOR DEPOSITION

Quarterly Report -- First Quarter

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The following report conveys the progress made during the first quarterly period, from January 1, 1989 to March 31, 1989 for ONR Contract number N-00014-86-C-0838. During this quarter, the work has primarily focused on the epitaxy of Ge on GaAs. The achievements, with regards to the insitu cleaning of Ge and GaAs surfaces, are discussed. The results of Ge homoepitaxy case which has been used as a vehicle for the optimization of the Ge/GaAs heteroepitaxy are discussed. We have studied the effects of adding hydrogen to the reagent gas mixture in an attempt to improve the mobilities of the Ge atoms on the surface. An additional aspect of the program addressed in this quarter has been the study of sub-cutaneous oxidation and its relevance to the gating of Ge.

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1.0 INTRODUCTION

The following report conveys the progress made during the first quarterly period, from January 1, 1989 to March 31, 1989 for ONR Contract number N00014-86-C-0838. Funding for the program is provided by the Strategic Defense Initiative under the Innovative Science and Technology through the Office of Naval Research. This program is a joint effort between the Research Triangle Institute's Center for Semiconductor Research and the North Carolina State University Physics department.

The program is focussed on the development of Ge/GaAs heterojunction High Mobility Transistor (HMT) technology. Briefly, such a technology would involve a Ge/GaAs heterojunction, where the carriers would be confined near the interface *in the Ge* due to the potential well created. This confined sheet of charge in the Ge at the interface serves as the channel in the FET structure. The design of such a device structure is basically aimed at harnessing the high mobilities of the carriers in this *2-d* carrier gas. Since mobilities are primarily governed by the scattering events, ideally, such a structure calls for low unintentional doping levels (near intrinsic) on GaAs with minimal interdiffusion effects at the interface.

During this quarter the work has primarily focussed on the epitaxy of Ge on GaAs. The removal of native oxides prior to deposition is an essential step for epitaxy. Section 2.0 highlights the achievements with regards to the *in situ* cleaning of Ge and GaAs surfaces. Reflection High Energy Electron Diffraction (RHEED) examinations, giving an insight into the physical nature of the surface, have been

complemented with in situ Auger analyses giving chemical information of the surface. Section 3 summarizes the results of Ge homo-epitaxy case which has been used as a vehicle for the optimization of the Ge/GaAs hetero-epitaxy. At the low growth temperatures ($\sim$ 300 °C) the unintentional doping levels were about 2E16 cm^{-3}. We have studied the effects of adding hydrogen to the reagent gas mixture in an attempt to improve the mobilities of the Ge atoms on the surface. While improved epitaxy has been observed with hydrogen addition, cross-contamination from multiple processing in the same reactor can be especially severe in these processes unless the chamber is adequately reconditioned. Section 4 summarizes the results of the Ge on GaAs hetero-epitaxy. The Ge/GaAs layers showed high unintentional doping levels accompanied with gross interdiffusion effects at the interface. Preliminary observations lead us to believe that residual hydrogen following the in situ clean causes erosion of the GaAs leading to the incorporation of the As in the film. An extensive Ar purge following the in situ clean has shown lower unintentional doping levels ($\sim$ 4E16 cm^{-3}).

An additional aspect of the program addressed in this quarter has been the study of sub-cutaneous oxidation and its relevance to the gating of Ge. Evidence is presented in Section 5.0 that suggests that oxidation of the underlying semiconductor substrate occurs during remote plasma deposition of SiO_2.

2.0 IN SITU CLEANING

Native oxides on semiconductor surfaces are normally amorphous in nature. The removal of native oxides prior to deposition is therefore critical to low

temperature epitaxy. We have used wet chemistry procedures to produce thin (~ 10 Å), controllable oxides prior to loading. This is then followed by an in situ cleaning treatment where *remotely* excited hydrogen is used to remove the residual oxides and produce clean, well-ordered surfaces prior to deposition. Previously reported in situ cleaning work used RHEED analysis to characterize the cleaned surfaces. In particular, reconstruction of the surface was used to verify the effectiveness of the cleaning process. Additional work has been done to chemically analyze surfaces of Ge and GaAs after the in situ cleaning with in vacuo Auger analysis. Analysis of in situ cleaned Ge and GaAs surfaces are shown in Figures 1 and 2 respectively. In both cases the carbon and oxygen have been removed from the semiconductor surface to within the detection limits of the Auger technique.

3.0 Ge HOMO-EPITAXY

The epitaxy of Ge on Ge(100) was studied to serve as a vehicle for the optimization of the hetero-epitaxy of Ge on GaAs(100). The addition of a vacuum load-lock to the system has ensured a consistently clean deposition environment. Besides, the enhanced throughput has allowed for the thorough investigation of all the deposition parameters to optimize the process.

The Ge layers were deposited at temperatures between 250 and 400 °C with the remote plasma-enhanced chemical vapor deposition (RPECVD) technique where GeH_4 was introduced *downstream* of an Ar (noble gas) discharge. Prior to deposition, the substrate surfaces were subjected to the in situ hydrogen treatment, as outlined in the previous section, to remove the native oxides. RHEED observations

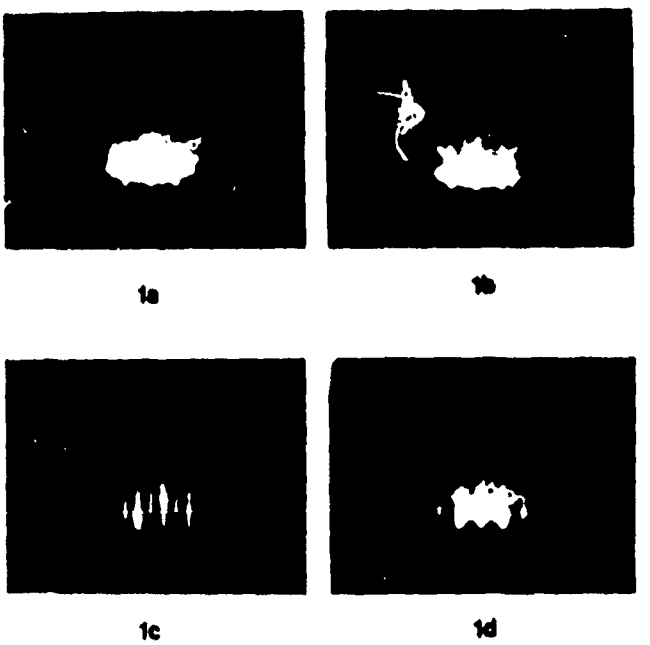


Figure 1. Hydrogen plasma treatments: (a) Ge(III) prior to treatment, (b) Ge(III) after 10s treatment, (c) Ge(III) after 20s treatment, (d) Si(100) after 10s treatment.

FIGURE 1a: Hydrogen plasma treatments: (a) Ge(111) prior to treatment. (b) Ge(111) after 10s treatment. (c) Ge(111) after 20s treatment. (d) Si(100) after 10s treatment.]

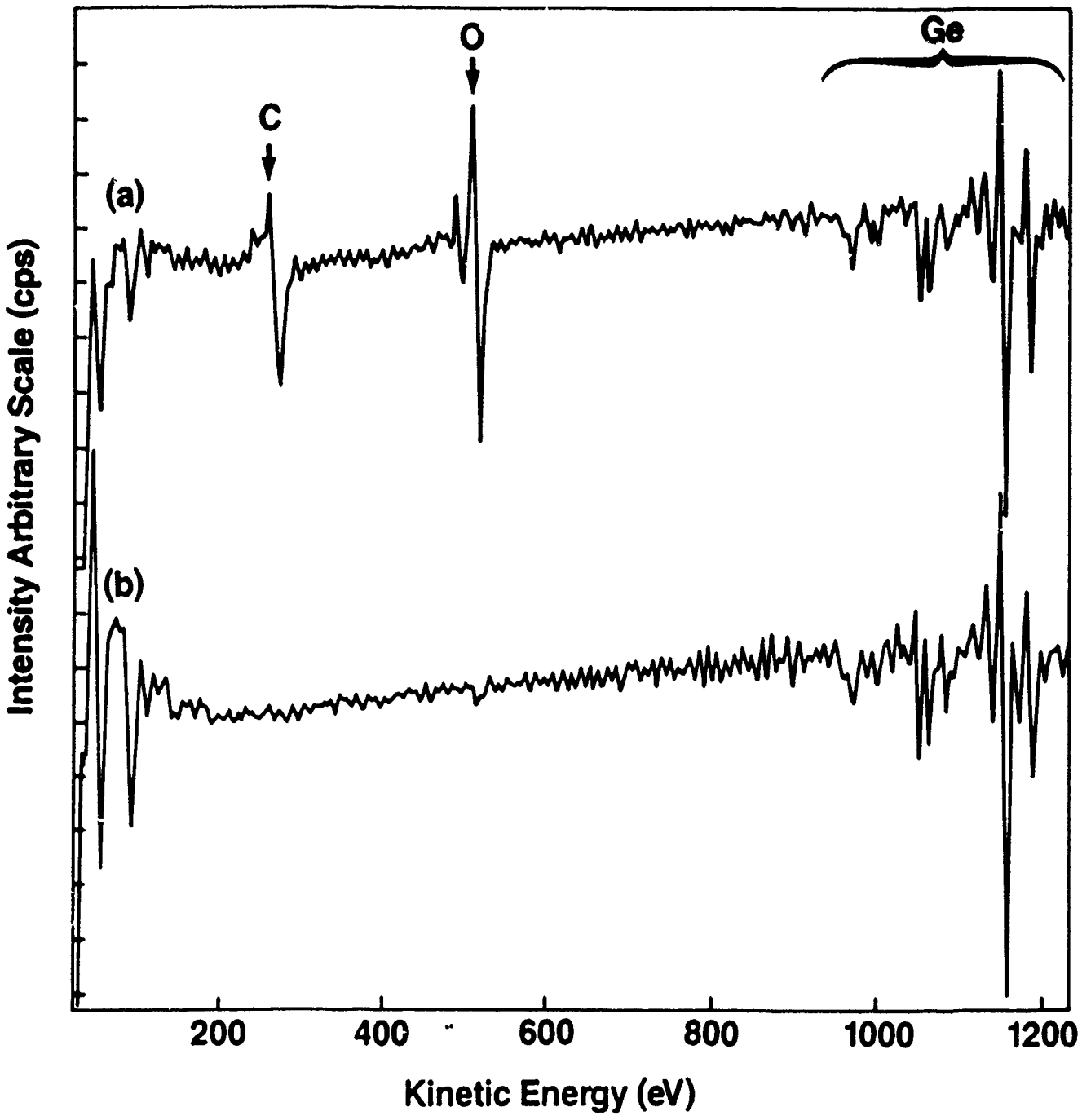
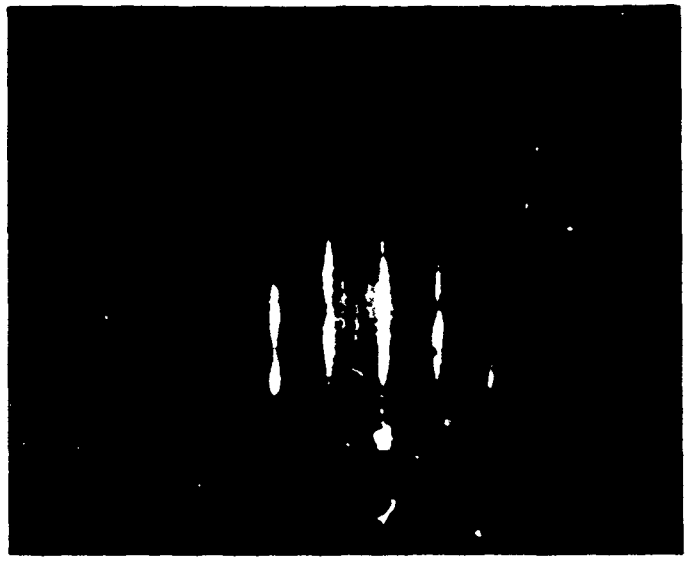


FIGURE 1b: In situ Auger analysis of the Ge surface showing the removal of oxygen and carbon following the surface cleaning treatment.

a

GaAs Before Hydrogen Treatment



b

GaAs After Hydrogen Treatment

FIGURE 2a: In situ Rheed analysis shows reconstructed GaAs following the surface cleaning treatment.

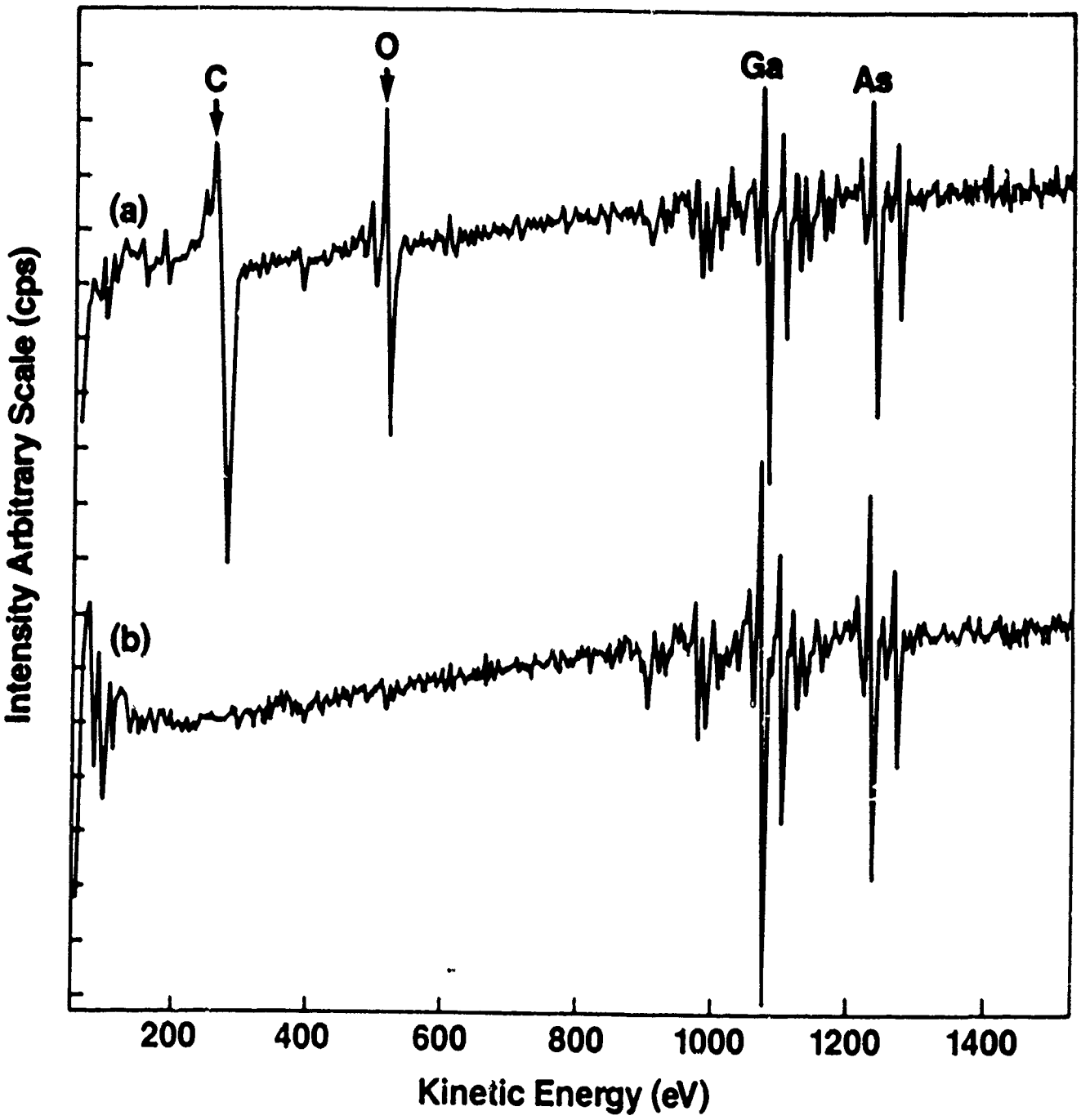


FIGURE 2b: In situ Auger analysis of the Ge surface showing the removal of oxygen and carbon following the surface cleaning treatment.

show that the deposited layers were single-crystalline in nature. The epitaxial quality was further evaluated with Rutherford Backscattering Spectrometry (RBS) measurements (Table 1). Spreading resistance measurements show that the as-deposited Ge layers are generally *n* type with a carrier concentration of about 2E16 cm^{-3}. Rapid thermal annealing at 650 °C for 10 s did not change this concentration, leading to the observation that the donors are at the substitutional sites at the growth temperature itself.

At temperatures as low as 300 °C, the mobility of the atoms is drastically reduced. Ge bonded to H is believed to have higher mobility than atomic Ge, especially at these lower temperatures. We have therefore investigated the addition of H_2 gas to the GeH_4 flow during deposition. This is believed to increase the mobility of the Ge atoms on the surface leading to improved film quality in the following way. The Ge deposition is proposed to occur in the following mode:

$$Ar^* + GeH_4 \longrightarrow Ar + GeH_X \quad \text{(GasPhase)}$$

$$GeH_X + -Ge- \longleftarrow Ge-Ge + H_2 \quad \text{(Surface)}$$

The addition of H_2 therefore slows the surface decomposition of GeH_X and therefore the rate of the Ge deposition. The persistence of Ge as GeH_X on the surface therefore translates into higher mobility for Ge.

TABLE 1:

RBS Analysis of Ge Homo-epitaxy

Sample	Growth Temperature (C)	X_{min} (%)
Without H2 Dilution		
n-Ge Standard	-	3.8
Ge-032189-1-Ge	250	(poly)
Ge-031789-2-Ge	300	3.7
Ge-032089-1-Ge	350	3.8
Ge-032189-2-Ge	400	3.9
With H2 Dilution		
Ge-032389-2-Ge	250	16.0
Ge-032289-1-Ge	300	4.0
Ge-032289-2-Ge	350	3.8
Ge-032389-1-Ge	400	3.9

Nominal Growth Conditions	
Plasma Feed	200 sccm Ar
Ring Feed	100 sccm Ar
	20 sccm GeH4
RF Power	30 Watts
Pressure	0.063 Torr

RHEED observations have clearly shown that the addition of hydrogen does improve epitaxy. Furthermore, the improved mobility of the atoms allows for the epitaxial deposition temperature to be driven lower than in the case without hydrogen. RBS results from the two cases are summarized in Table 1 and Figure 3.

While hydrogen dilution shows improved epitaxy, it can also bring problems especially when multiple processing is performed in the same chamber. Figure 4 shows SIMS analysis on a Ge homo-epitaxial layer grown with the addition of hydrogen to the reactant gas mixture. The layer shows a build-up of Si and O starting from the interface through the bulk of the layer. Also shown is an analysis of a Ge layer grown without hydrogen dilution, but with a hydrogen in situ clean prior to growth. Notice the build up of Si and O at the interface along with the H signal. This is believed to be originating from the reaction of the reactive atomic hydrogen with SiO_2 wall deposits from earlier oxide deposition sequences. This observation calls for reactor conditioning prior to deposition sequences. We have observed that extended Ar plasma treatments assist in removing some of the loosely bound (especially the OH groups) reactive by-products of oxide deposition sequences.

4.0 Ge HETERO-EPITAXY ON GaAs

The epitaxy of Ge on GaAs is certainly assisted by the fact that the lattice mis-match between the two crystalline materials is less than 0.2%. Unlike the homo-epitaxy case, the Ge hetero-epitaxy case is compounded by problems due to

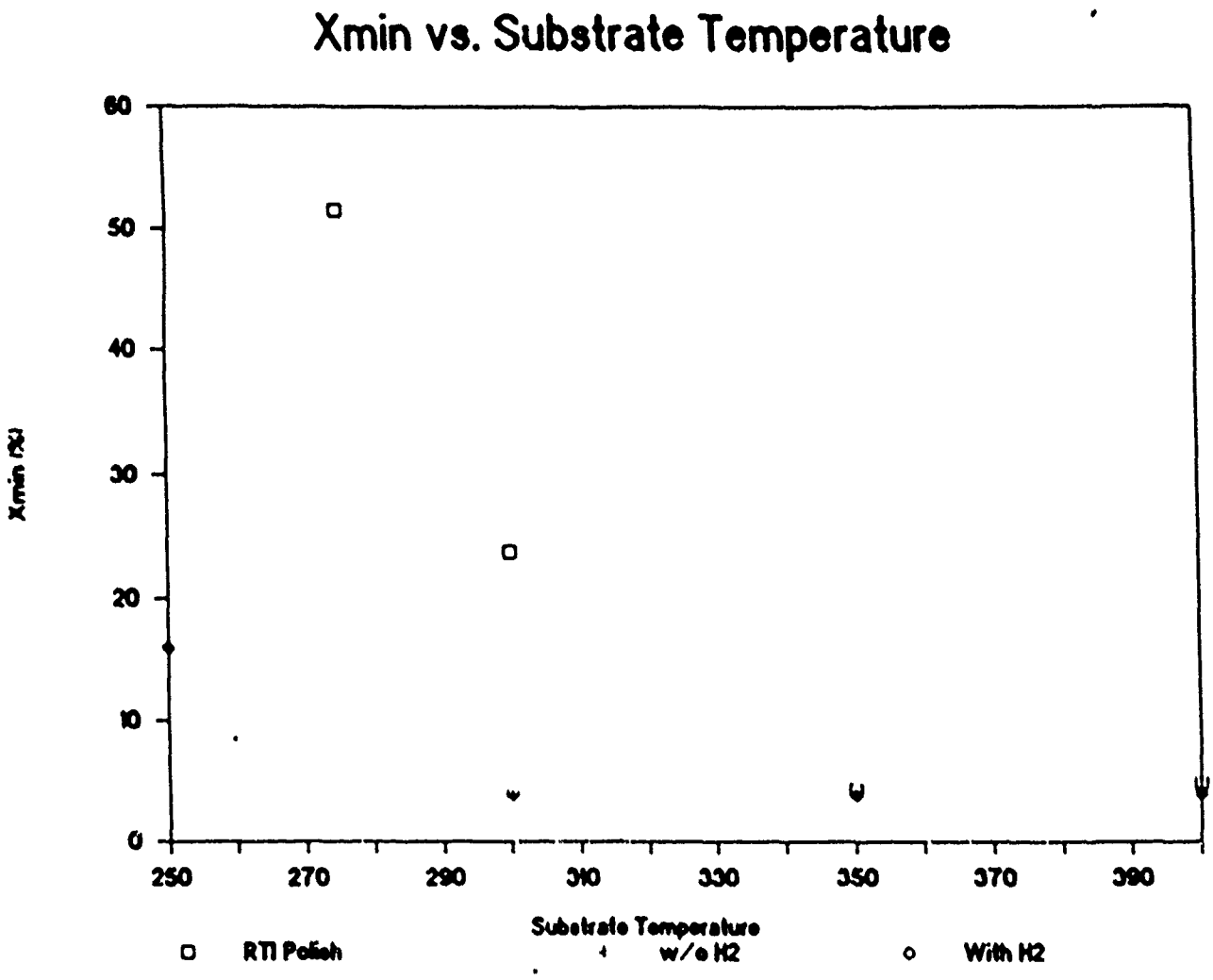


FIGURE 3: RBS channelling data showing the variation of $X_{min}(\%)$ versus substrate temperature. Note the minimum at 350 °.

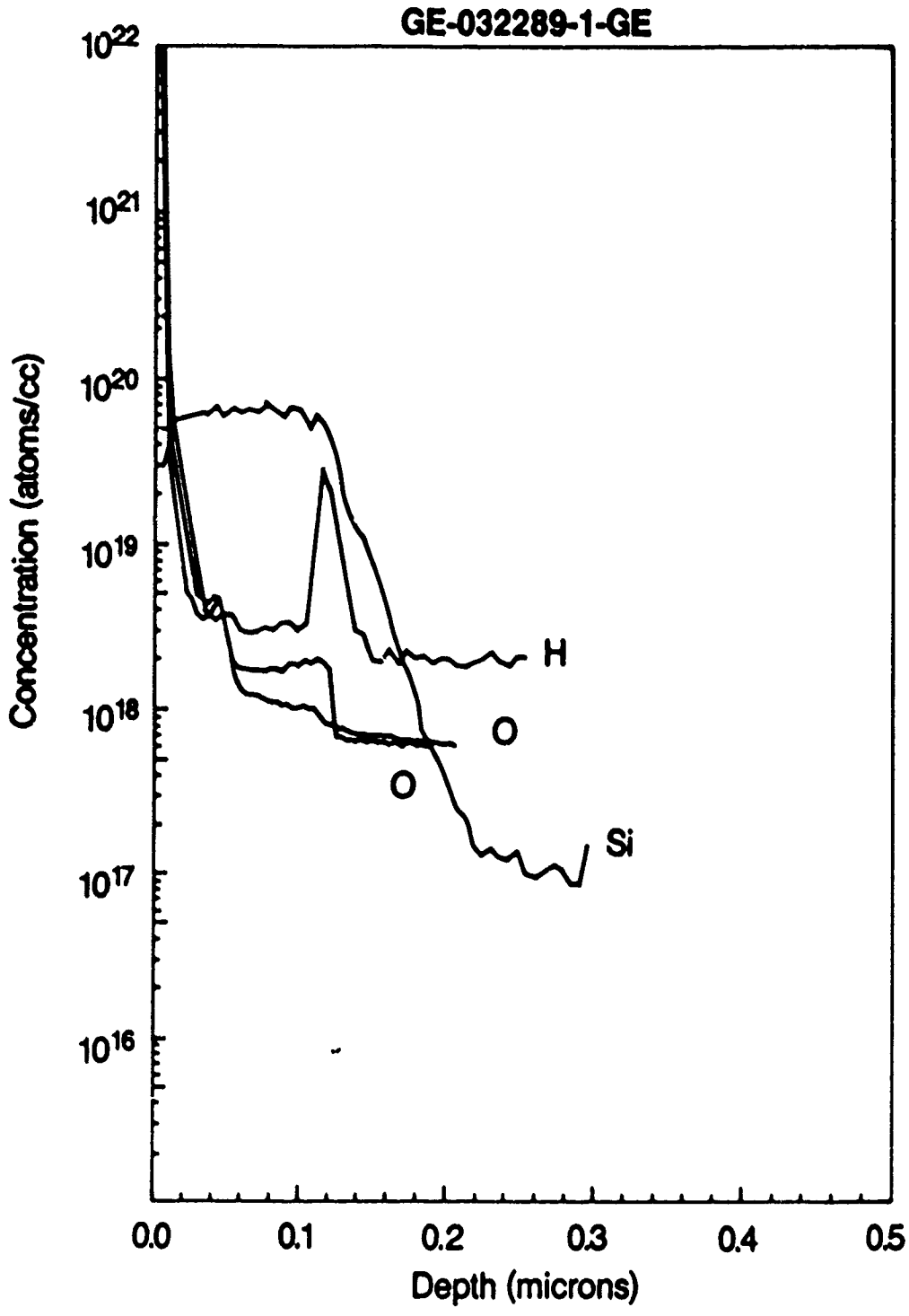


FIGURE 4a: SIMS analysis: H_2 dilution improves epitaxy, but can cause cross-contamination with multiple processing. Figure shows buildup of O and Si in the epitaxial layer with H_2 dilution. This calls for reactor reconditioning prior to growth.

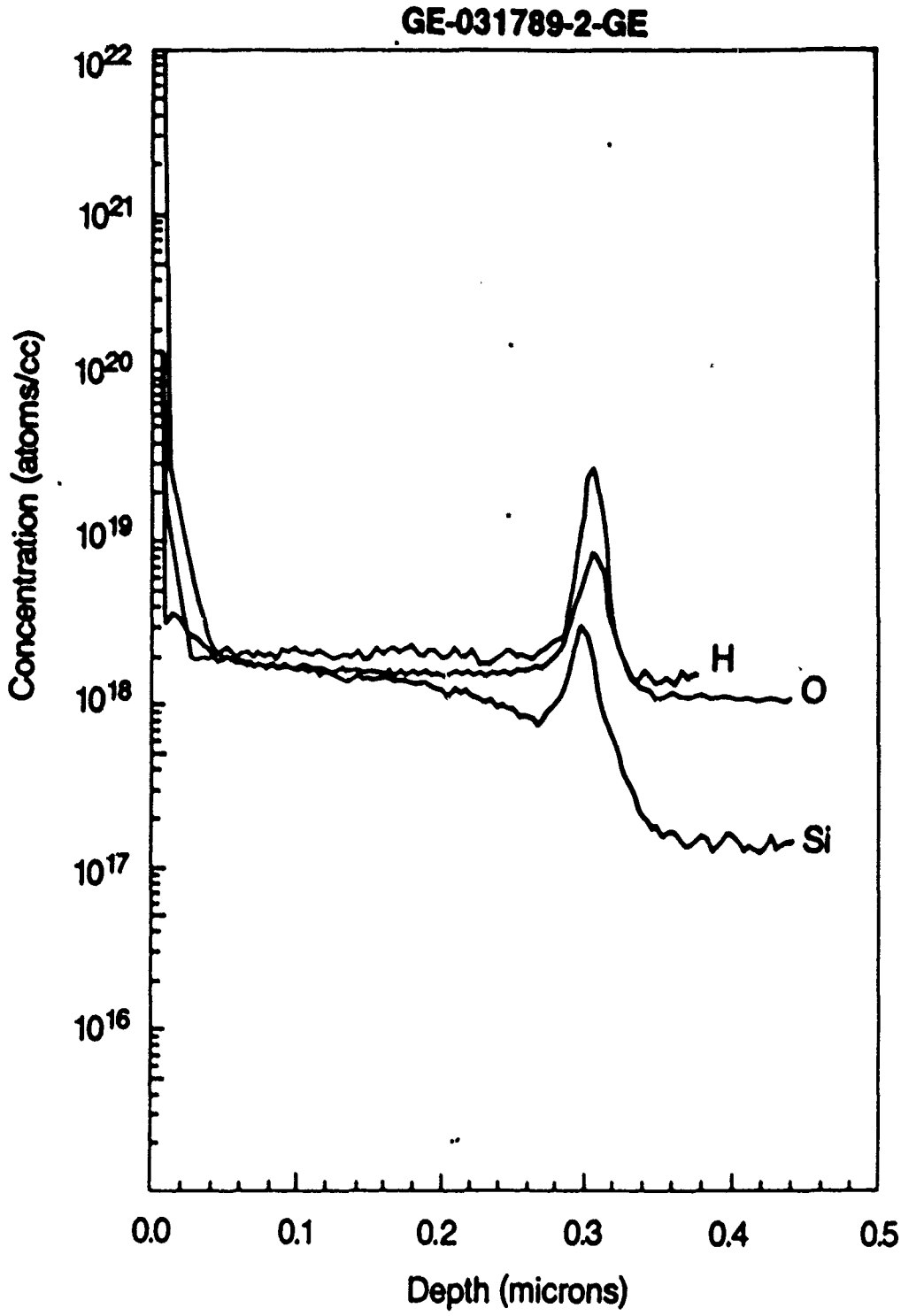


FIGURE 4b: Unless the reactor is reconditioned, the active hydrogen duriing the in situ clean can react with wall deposits to contaminate the interface as seen in this figure.

the high As vapor pressure. This leads to undesirable interdiffusion effects at the interface.

Prior to deposition, the GaAs was subjected to the in situ cleaning treatment. The Ge depositions were performed at low pressure (about 70 mTorr) at temperatures ranging from 250 to 400 °C. The depositions were targeted at obtaining low unintentional doping levels with minimum interdiffusion at the interface. Table 2 shows Hall measurements on some of the Ge/GaAs Increasing the growth rate shows a remarkable decrease in the unintentional doping level. Increase in the growth temperature (from 300 to 350 °C) shows an increase (undesirable) in the unintentional doping while improving the mobility. It was thought that residual hydrogen remaining after the in situ clean may continually etch the GaAs surface resulting in As incorporation in the growing film. An Ar purge following the in situ clean (to sweep away any residual hydrogen) following the in situ clean showed dramatic decrease in the unintentional impurity level. It was also thought that any hydrogen adsorbed on the GaAs surface following the in situ treatment may again etch the GaAs with consequent incorporation of As in the film. Heating of the substrate to 375 °C (in vacuo) following the in situ treatment also reduced the unintentional doping level. However, the Ar purge seems to have made the most beneficial effect.

Spreading resistance measurements were also performed to corroborate the above observations. Figure 5 shows the unintentional doping level in a *homoepitaxial* Ge film (about 2E16 cm $^{-3}$) grown at 350 °C. The following Figure 6

TABLE 2 Hall Measurements On Ge Layer Grown On Semi-Insulating GaAs

Sample No.	Growth Temp C	Carrier Concn. cm-3	Carrier Mobility cm2/Vs	Growth Rate A/min	GeH4 Flow sccm	COMMENTS
1	300	1.0E+19	138.0	6.8	5	Slow growth rate
2	300	1.8E+18	163.2	27.7	20	Fast growth rate
3	350	2.0E+18	288.0	29.3	20	High temp. growth
4	300	1.1E+18	68.8	27.7	20	Substrate heated to 375 C after in situ clean
5	300	4.0E+17	135.5	27.7	20	Ar purge following in situ clean

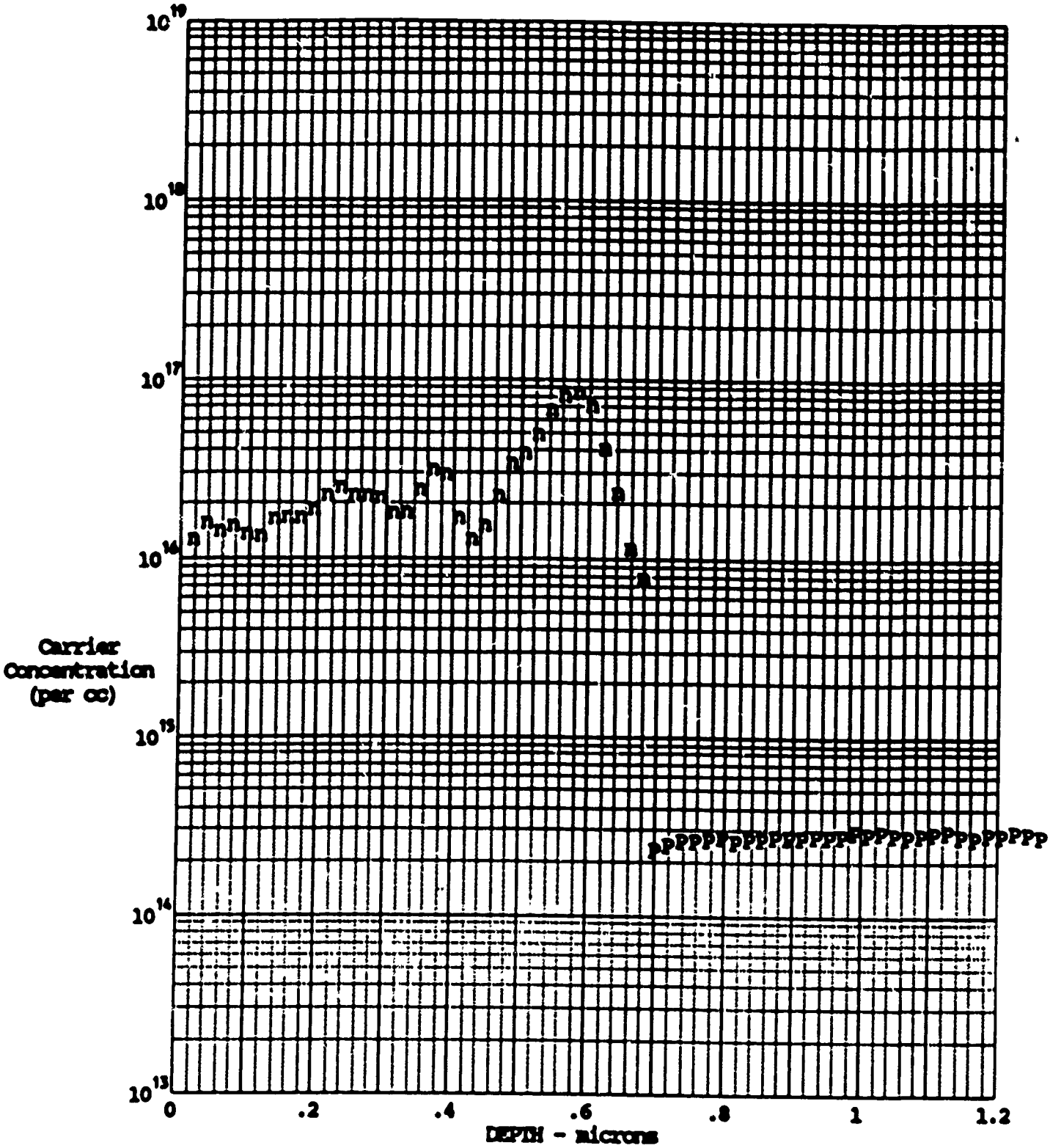


FIGURE 5: Carrier profile from spreading resistance measurements on a Ge homo-epitaxial layer. Shows an unintentional doping level of about 2E16cm $^{-3}$.

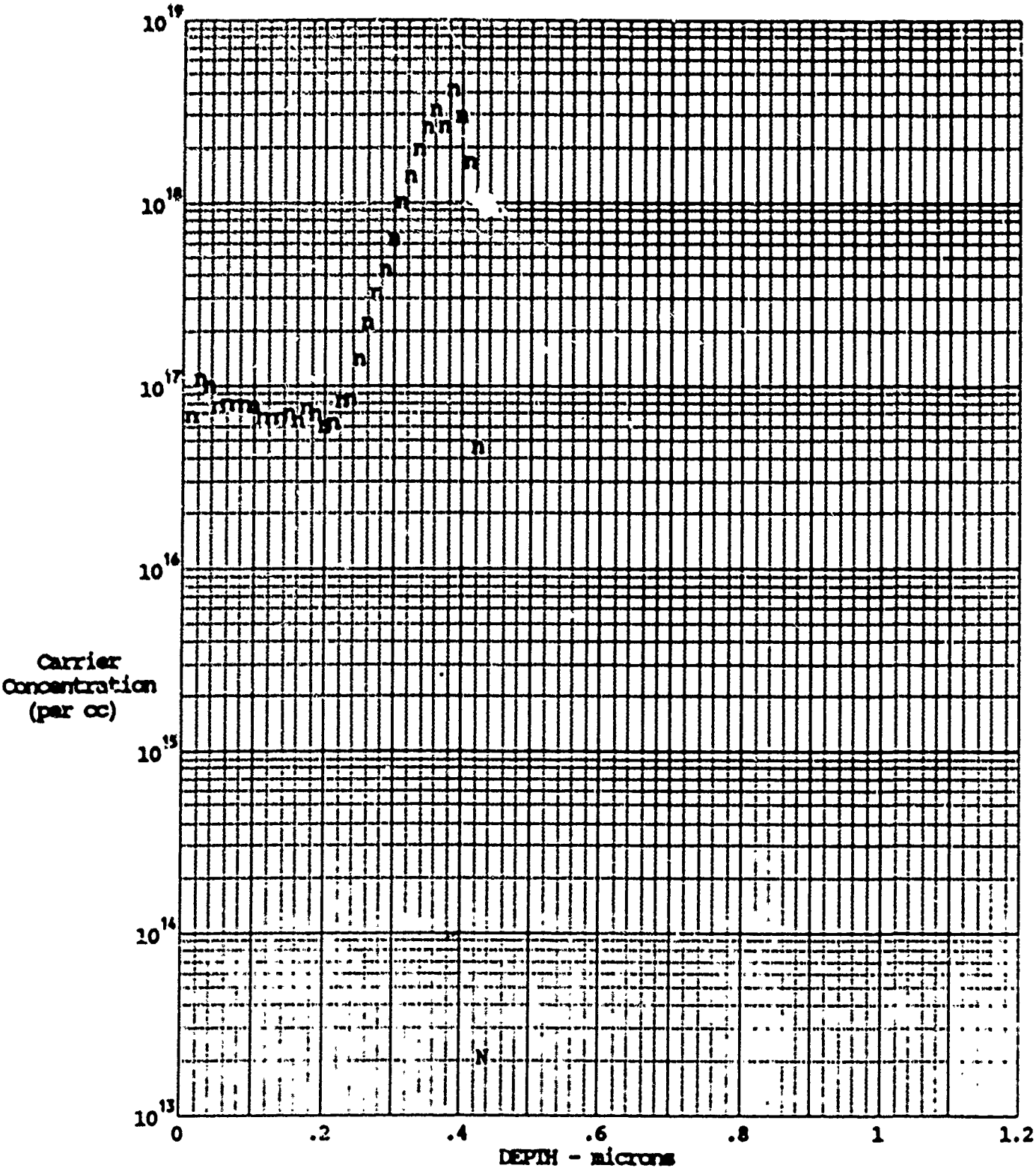


FIGURE 6: Carrier profile in a Ge layer on GaAs grown at 300 C. The layer shows interdiffusion and high unintentional doping suspected to be due to etching of GaAs by residual hydrogen following in situ clean.

shows the carrier profile in a hetero-epitaxial Ge/GaAs film grown at 300 °C. Note that the electron concentration is the highest at the interface and drops to about 1E17 cm^{-3} near the surface. An inference is appropriate at this point: the carrier concentration drops within the first 200 nm and then stays almost flat through the rest of the layer up to the surface. This suggests that residual hydrogen from the in situ clean may indeed be causing the erosion of the As from the surface (with resulting incorporation into the film) until such a time that all the residual hydrogen is swept away. Rapid thermal anneal of the sample only broadened the peak. Figure 7 shows that the unintentional doping is reduced with heating the substrate to 375 °C after the in situ hydrogen clean. Figure 8 shows that an Ar purge following the in situ clean gives the lowest unintentional doping levels (closest to that obtained with in the homo-epi case) with minimum interdiffusion.

5.0 SUB-CUTANEOUS OXIDATION

The pseudomorphic Si SiO_2 insulator structure developed under this program has enabled successful gating of Ge surfaces. Since oxides of Ge are leaky and highly unstable, we use the thin, *pseudomorphic* Si interlayer between the Ge and the SiO_2. Both the Si and the SiO_2 are deposited with the remote plasma technique. The Si layer prevents any subsequent oxidation of the underlying Ge and also forms an excellent interface with SiO_2. The original intended purpose of the the pseudomorphic Si interlayer in the Ge-Si-SiO_2 MIS structure was to prevent oxidation of the Ge surface during the first moments of the oxide deposition when the semiconductor surface is exposed directly to excited oxygen. We have since

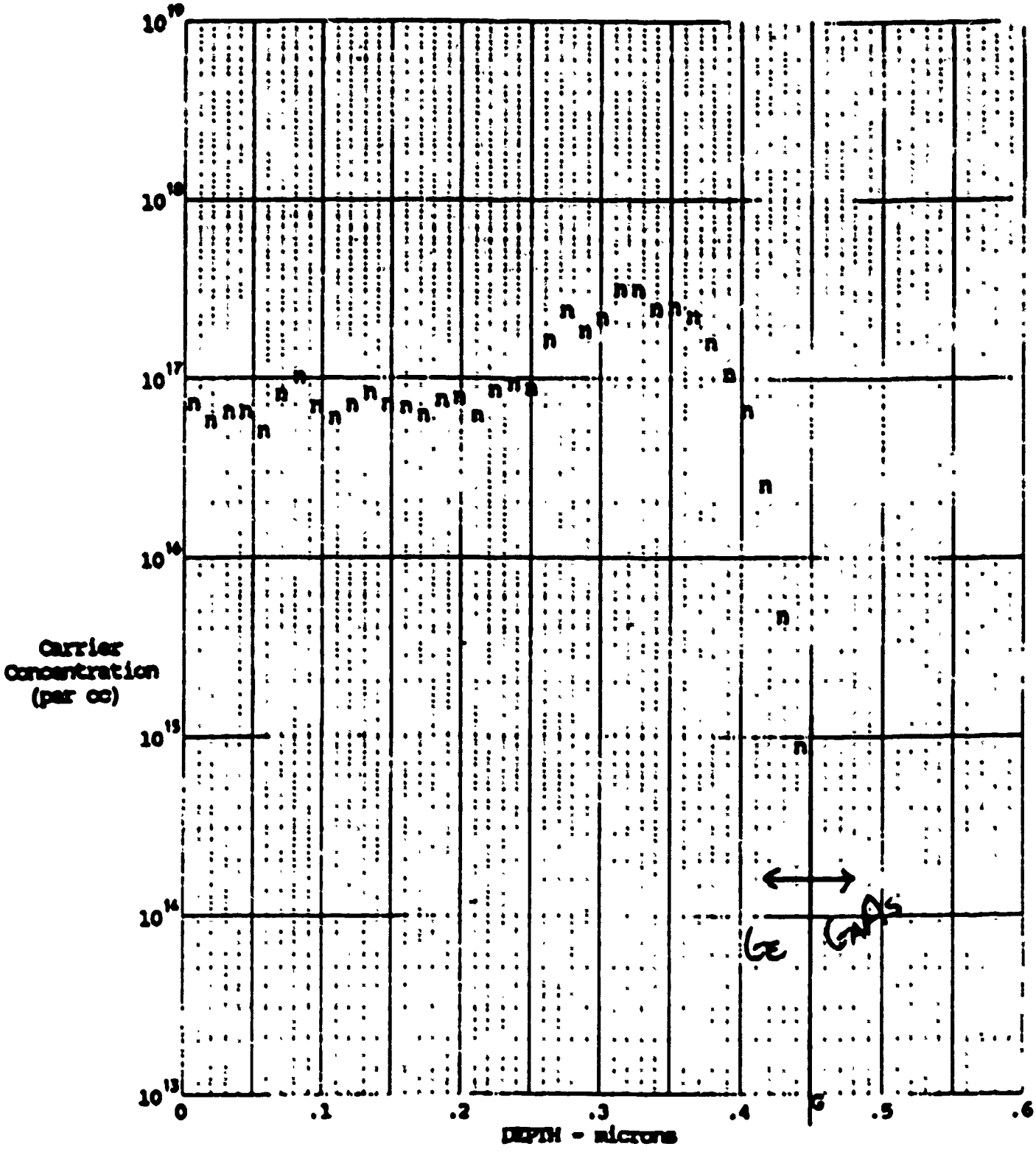


FIGURE 7: Heating the substrate at 375 °C in vacuum is seen to reduce the unintentional doping.

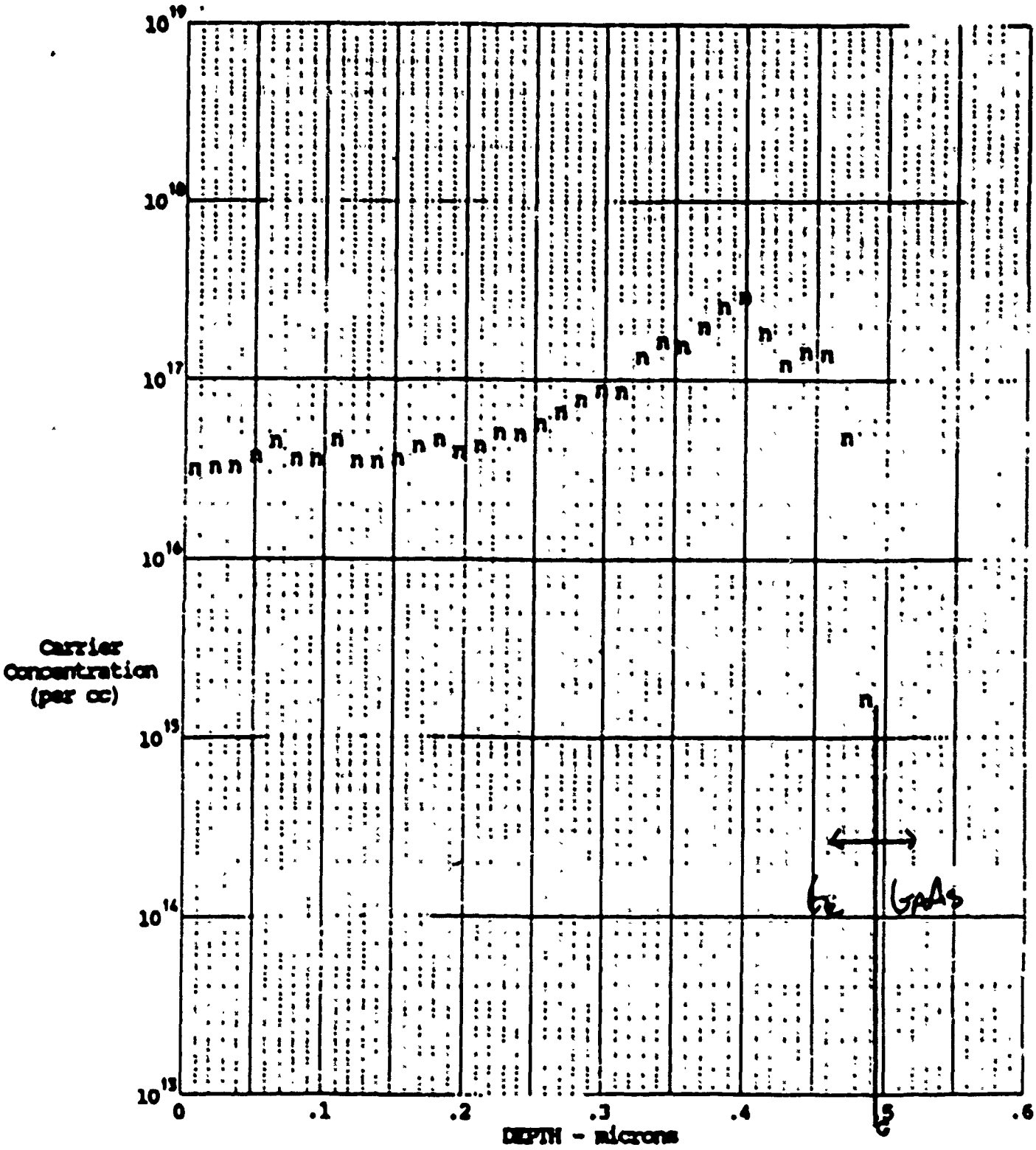


FIGURE 8: An Ar purge following the in situ clean gives the lowest unintentional doping and minimum interdiffusion at the interface.

concluded that additional subcutaneous oxidation takes place beneath the depositing oxide film throughout the deposition process. While the composite insulator structure has shown remarkable results in the gating of Ge, we recognize that the optimal design of this structure depends on the sub-cutaneous oxidation rate, viz. the rate at which the underlying Si is oxidized. Evidence is presented in Appendix A which indicates that oxidation of the underlying semiconductor surface occurs during RPECVD deposition of the SiO_2 layer. This phenomenon has implications in the process design of this novel structure, in that it places a constraint on the thickness of the SiO_2 layer for a given thickness of the Si interlayer or vice versa.

6.0 SUMMARY AND PREVIEW

During the first quarter, January to March 1989, the program efforts were focussed on the epitaxy of Ge on GaAs. A viable technology was developed for the the in situ cleaning of Ge and GaAs surfaces prior to epitaxy. Progress was made in both the homo-epitaxy on Ge and the hetero-epitaxy on GaAs. The best unintentional doping achieved to date has been 2E16 cm^{-3}. Interdiffusion has been significantly reduced by introducing an Ar purge following the in situ cleaning step.

During the next quarter, work on the pseudomorphic insulator structure will continue. A new mask set for MISFET and MIS capacitor structures will be fabricated and put to use.